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ANTICORROSIVE COPPER ALLOY FOR OCEAN USE  
[海洋用耐食銅合金]

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APPLICANT(S)	(71):	MITSUI MINING & SMELTING CO., LTD.
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TITLE	(54):	ANTICORROSIVE COPPER ALLOY FOR OCEAN USE
FOREIGN TITLE	[54A]:	海洋用耐食銅合金

## SPECIFICATION

### 1. Title of the Invention

Anticorrosive Copper Alloy for Ocean Use

### 2. Scope of Patent Claims

(1) An anticorrosive copper alloy for ocean use, comprising of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, the remaining parts of copper, and unavoidable impurities, which is a characteristic of the restraining dezincification phenomenon.

(2) An anticorrosive copper alloy for ocean use, comprising of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, 0.05 to 0.5% by weight of Ni, the remaining parts of copper, and unavoidable impurities, which is a characteristic of the restraining dezincification phenomenon.

### 3. Detailed Description of the Invention

[Industrial Application Field]

The present invention relates to an anticorrosive copper alloy, which is used for a wire net for a fish pen, a lattice for a sluice gate, a cover for a steel stake, and the like, in an ocean environment and has both properties for anti-algae and dezincification.

[Prior Art]

Generally, anticorrosive metal materials, used in the ocean or a situation contacting a tidal zone, demand functions such as a strength to correspond to individual uses, as well as organisms sticking less, such as shellfish and algae (hereafter, referred to as antialgal properties).

To secure the antialgal properties, a method to apply coating materials containing tin compounds has been conventionally known. Recently, nickel silver, as typified in 90 Cu - 10 Ni alloy, tends to be used as materials for a fish pen, a lattice for a sluice gate, and the like. This method utilizes an action that can avoid attaching organisms, such as shellfish and algae, due to the influence of Cu ions that liquate out into seawater.

However, the former method to coat coating materials containing tin compounds cannot avoid the problems of the coating materials, such as deterioration, longevity, and poor construction, and thus is hardly expected to have a long life. In contrast, nickel silver is superior in both antialgal and anticorrosive properties but has a defect that is, an anticorrosive membrane is getting thicker in a several years, the quantity of liquation of Cu ions decreases, and thus algae easily attach. Moreover, the price of bullion is high, and thus the use of nickel silver is limited.

On the contrary, if brass, which costs cheaper, is used in the ocean, it shows superior antialgal properties but causes dezincification corrosion. Thus its strength lowers over time, and it will be unsuitable for use. Accordingly, development of an anticorrosive alloy for ocean use has been desired.

[Objective of the Invention]

The objective of the present invention is to provide an anticorrosive copper alloy for ocean use, which prevents the dezincification corrosion that brass causes as mentioned above, secures a long-term liquation of copper ions, has antialgal properties, and is superior in both general anticorrosion and strength.

[Problems to Be Solved by the Invention]

The present invention was completed to achieve the above-mentioned objective. For embodiment, when a copper alloy is used for creating a wire net for a fish pen, the desirable characteristics are as follows:

- (1) Copper ions liquate from materials for a fish pen for a long time in order to secure the antialgal properties.
- (2) When the liquation of copper ions is secured, make sure that the quantity of liquation does not become too much. That is, its life becomes short due to

insufficient anti-corrosivity.

- (3) Selective leaching phenomenon, such as dezincification corrosion, is not caused.
- (4) The strength is so high as to endure a typhoon and the like, and thinning is capable.
- (5) Its process-ability is good.
- (6) Local corrosion hardly occurs.
- (7) Its ingredients are cheap.

[Means to Solve the Problems]

The present inventors have eagerly studied the relationships between ingredients of an anticorrosive alloy for ocean use and the aforementioned desirable ingredients and thus obtained the following knowledge to complete the invention. First, Zn is effective to raise the strength of alloy and to lower the prices of the raw materials. When Zn is added, the quantity of liquation of the copper ions gradually decreases but not so much as to exert a baneful influence and is rather favorable. However, since adding Zn causes dezincification corrosion, a countermeasure is necessary. That is, if Zn is less than 20% by weight, the above-mentioned advantage is not obtained sufficiently; if it is more than 37% by weight, the process-ability of alloy decreases, and dezincification corrosion becomes considerable.

Al has actions to raise the strength of the alloy, to restrain the liquation of copper due to the addition of Sn and P, and to secure the anti-corrosivity. If Al is less than 0.05% by weight, this effect is insufficient; if it is more than 0.5% by weight, strong membrane is easily caused on the surface of alloy, the quantity of liquation of copper ions extremely decreases while the time passes, faults are caused in antialgal properties, and the quantity of dezincification corrosion increases.

Sn is effective in restraining dezincification corrosion. If Sn is less than 0.05% by weight, this effect is insufficient; if it is more than 0.4% by weight, its effect is saturated, and its process-ability is damaged simultaneously.

Incidentally, Sn and P are effective in restraining dezincification corrosion respectively and show a multiplier effect to restrain dezincification corrosion when both of them are added.

Ni is effective in miniaturizing crystallized grains to enhance anti-corrosivity, as well as strength. Accordingly, when Ni is also added to the above-mentioned composition of alloy, Ni will further enhance the effects of the present invention. When the amount of Ni contained in the present invention was less than 0.05% by weight, this effect was few; if it was more than 0.5% by weight, dezincification corrosion was easily caused.

As mentioned above, the first anticorrosive copper alloy for ocean use as in the present invention comprises of 20 to 37% by weight of Zn, 0.05 to 0.5% by weight of Al, 0.05 to 0.4% by weight of Sn, 0.01 to 0.05% by weight of P, the remaining parts of copper, and unavoidable impurities. The second alloy comprises of the compositions of Zn, Al, Sn, and P as the ingredients in the first alloy, 0.05 to 0.5% by weight of Ni, the remaining parts of copper and unavoidable impurities and has a characteristic to potentially restrain the dezincification phenomenon.

The effects of the copper alloy by the present invention are described below on the basis of embodiments, also referring to comparison embodiments.

[Embodiments]

Copper alloys, which Table 1 shows, in graphite melting pots respectively were melted in a high-frequency melting furnace and were casted in metal moulds respectively. The lumps of ingot prepared were face-grinded and were repeatedly annealed and rolled until flat materials with the thickness of 1 mm at the finish, equivalent to half H materials wherein the rolling ratio was between 15% and 20%, were produced. The following experiments were conducted with these flat materials.

① The samples were attached to a rotating substance of a water wheel rotated by a speed of 2 m/s in natural seawater



and were left alone for 1,000 hours. The amount of corrosion was calculated with the differences between the weights of samples before and after the test, and was expressed with a unit of mg/day/dm<sup>2</sup>.

② As a dezincification test, the samples were soaked in a solution of CuCl<sub>2</sub>-2H<sub>2</sub>O (12.8 g/l) at 75 C on the basis of ISO standards for one day, and then the depth of corrosion at 10 spots on the sections of samples was found. The maximum values of depth were expressed in µm.

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③ 200 mm × 100 mm of test pieces were soaked in seawater for practical use at a depth of 70 cm for one year, and the situation where organisms attached was observed.

④ A tension test was conducted to measure the tensile strength and extension.

Table 1 shows these results below.

Table 1

	Sample No.	Composition of Alloy					Amount of Corrosion (mdd)	Amount of Dezincification (µm)	Antialgal Properties (Note)	Tensile Strength (Kgf/mm <sup>2</sup> )	Extension (%)
		Zn	P	Sn	Al	Ni					
Embodiment	1	34	0.03	0.22	0.08	0.09	480	75	o	55	16
Embodiment	2	34	0.04	0.22	.028	0.09	380	100	o	58	14
Embodiment	3	34	0.03	0.22	0.27	--	400	100	o	56	15
Embodiment	4	25	0.01	0.05	0.10	--	270	60	o	50	17
Embodiment	5	35	0.04	0.32	.038	--	240	110	o□	57	14
Comparative Example	6	30	--	--	--	--	250	440	o	46	35
Comparative Example	7	35	0.02	0.21	--	0.19	490	0	o	60	11
Comparative Example	8	32	0.04	0.22	0.59	0.10	180	150	x	62	9

Comparative Example	9	33	0.04	0.21	0.30	0.60	360	640	o	61	8
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Note) The antialgal properties are expressed with o: no

organisms attached; x: barnacles, ascidians, and the like  
covered more than a half of the surface, and Δ: a few  
organisms attached.

As Table 1 shows, the amount of corrosion increases under the existence of Sn and P that were added to prevent dezincification corrosion but also tends to decrease due to the addition of Al. Moreover, the amount of dezincification becomes 0 conversely due to Sn and P as Comparative Example 7 shows but increases a little due to the addition of Al. Furthermore, great amounts of additions of Al and Ni result in dezincification. While the amount of addition of Al increases, the antialgal properties decrease. For the tensile strength and extension, other alloys that have more ingredients added than Comparative Example 6 tend to show high strength and low extension, as well as show the effects of Al, Ni, and Zn.

In addition, the relationships between the amount of corrosion and that of dezincification, which were affected when Al was added to an alloy comprising of 34 to 35 of Cu, 0.02 to 0.04 of Zn, 0.21 to 0.22 of P, and Sn (and Ni), were plotted in Fig. 1 on the basis of the data of Table 1.

As Fig. 1 clearly shows, the alloy as the present invention restrains dezincification, as well as the amount of corrosion.

As Table 1 clearly shows, the alloy as the present invention prevents organisms, such as shellfish and algae, from attaching, due to liquation of Cu ions, increases the mechanical strength of brass to augment the reliability in strength, and can make a wire diameter narrow to decrease materials to be used and thus to further enhance the economical efficiency potentially.

[Effects of the Invention]

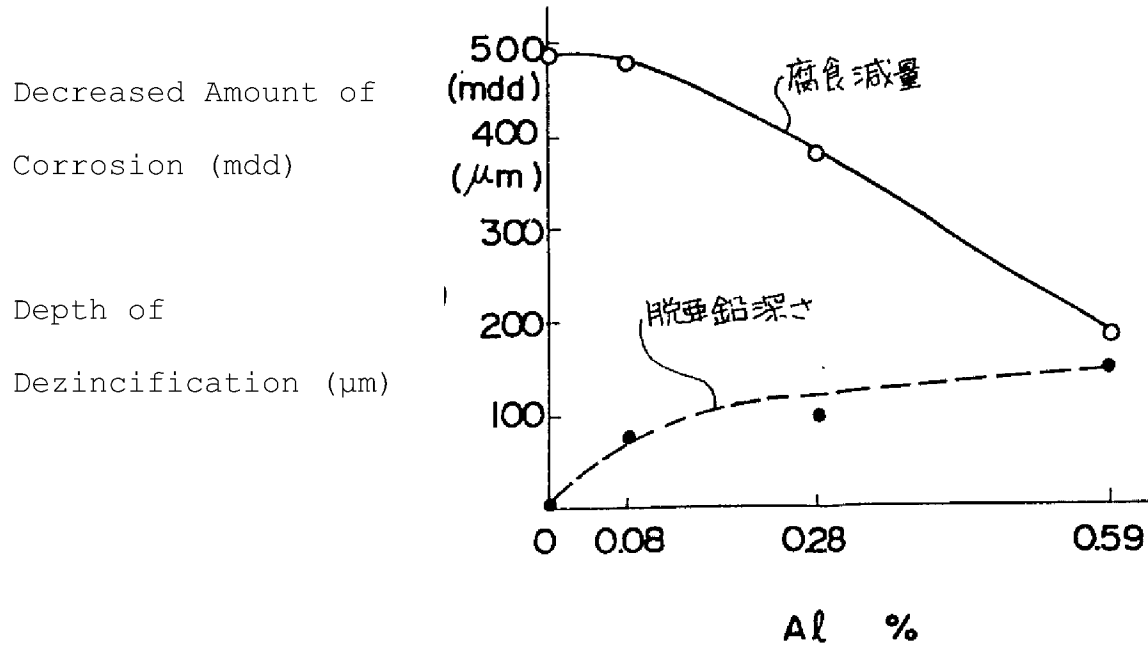
As Embodiments clearly show, the anticorrosive copper alloy as the present invention utilizes both superior properties for anticorrosion and anti-alga and is suitable as material for a lattice for sluice gate, a fish pen, a cover for steel stake, outer deck boards of shipping, and the like in the ocean environment or for devices to deal with seawater for use to avoid attaching organisms.

#### 4. Brief Descriptions of the Drawings

Fig. 1 is a graph, which shows both the decreased amount of corrosion and depth of amount of dezincification when Al was added to the present alloy and the like.

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Fig. 1



Amendment (Spontaneous)

To: Commissioner of the Patent Office

September 10, 1984 (Showa 59)

1. Description of the Present Case

Patent Application No. 59-168764

2. Title of the Invention

Anticorrosive Copper Alloy for Ocean Use

3. Person making Amendment

Relationship to the Case: Patent Applicant

Title (Name): (618) Mitsui Mining & Smelting Co., Ltd.

4. Representative

Address: Shuwa Dai 2 Toranomom Building

21-19 1-Chome Toranomom, Minato Ward, Tokyo

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Name: Attorney (6073) Saburo Kimura

5. Date of ( ): Year Month Day

(Sent on: Year Month Day)

6. Objects for the Amendment

Column of "Detailed Description of the Invention" in the Specification

7. Contents of the Amendment

(1) Amend the "due to addition of Sn and P" on line 17, page 4 of the Specification to "caused from addition of Sn and P".

(2) Amend "Incidentally, Sn and P are ... show ..." on lines 7 to 9, page 5 of the Specification to "P is effective to restrain dezincification corrosion; if it is less than 0.01%, the effect is insufficient; if it is more than 0.05%, the effect is saturated, as well as the process-ability becomes poor simultaneously.

Incidentally, Sn and P show a multiplier effect to restrain dezincification corrosion when both of them are added".

(3) Amend "of water wheel" on line 13, page 6 of the Specification to "like a water wheel".

(4) Amend "75 C" on line 17, page 6 of the Specification to "75°C".

(5) Amend the values in the columns of "Amount of corrosion (mdd)" on Table 1 on page 8 of the Specification respectively as follows:

"480" → "48"

"380" → "38"

"400" → "40"

"270" → "27"

"240" → "24"

"250" → "25"

"490" → "49"

"180" → "18"

"360" → "36"

# PATENT ABSTRACTS OF JAPAN

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(51)Int.Cl.

C22C 9/04

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(71)Applicant : MITSUI MINING & SMELTING CO  
LTD

(22)Date of filing : 14.08.1984

(72)Inventor : HASEGAWA HIROMICHI  
YAMAGUCHI HIROSHI

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## (54) CORROSION RESISTANT COPPER ALLOY FOR OCEAN

### (57)Abstract:

PURPOSE: To obtain a corrosion resistant Cu alloy for the sea provided with resistance to dezincification and fouling by seaweeds by adding specified amounts of An, Al, Sn and P to Cu so as to inhibit a dezincification phenomenon.

CONSTITUTION: The composition of a Cu alloy is composed of, by weight, 20W 37% Zn, 0.05W0.5% Al, 0.05W0.4% Sn, 0.01W0.05% P and the balance Cu with inevitable impurities. 0.05W0.5 Ni may be added to the composition. The Cu alloy has dezincification resistance and superior resistance to fouling by seaweeds.

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## LEGAL STATUS

[Date of request for examination]

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昭61-48547

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6411-4K

審査請求 未請求 発明の数 2 (全4頁)

⑮ 発明の名称 海洋用耐食銅合金

⑯ 特 願 昭59-168764

⑰ 出 願 昭59(1984)8月14日

⑱ 発 明 者 長 谷 川 博 理 上尾市大字今泉262-12

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㉑ 代 理 人 弁理士 木村 三朗 外1名

明 細 書

1. 発明の名称

海洋用耐食銅合金

2. 特許請求の範囲

(1) Zn 20～37重量%、Al 0.05～0.5重量%、Sn 0.05～0.4重量%、P 0.01～0.05重量%、残部銅及び不可避不純物からなる脱亜鉛現象を抑制したことを特徴とする海洋用耐食銅合金。

(2) Zn 20～37重量%、Al 0.05～0.5重量%、Sn 0.05～0.4重量%、P 0.01～0.05重量%、Ni 0.05～0.5重量%、残部銅及び不可避不純物からなる脱亜鉛現象を抑制したことを特徴とする海洋用耐食銅合金。

3. 発明の詳細な説明

〔産業上の利用分野〕

本発明は、いけす用金網、取水口格子、鋼杭のカバー等の海洋環境において用いる、防藻性と脱亜鉛性とを兼ね備えた耐食銅合金に関するものである。

〔従来の技術〕

一般に、海洋中又は干満帯等に接する状況で用いられる耐食金属材料には、個々の用途に対応する強度等の機能の他に、貝類、藻類等の生物付着が少ない(以下防藻性という。)ことが要求される。

これら防藻性を確保するためには、錫化合物を含む塗料を塗布する方法が従来知られているが、最近90 Cu-10 Ni合金に代表される白銅が、いけす材料や取水口格子等として用いられる動きがある。これは銅合金から徐々に海水中に溶出するCuイオンの影響で、貝や藻等の生物の付着が妨げられる作用を利用するものである。

然しながら前者の錫化合物を含む塗料の塗装法では塗料の劣化、寿命、施工不良等の問題が避けられず、長期間の寿命を期待することは難しい。また白銅は、防藻性、耐食性において優れているが、数年経過すると耐食性皮膜が厚くなつてCuイオンの溶出量が減少して藻が付き易くなる欠点がありまた地金価格が高く使用に限界がある。



一方コストが安い黄銅を海洋中で用いると防食性は優れているが脱亜鉛腐食を起し強度が時間の経過と共に低下し使用に適さなくなる等の問題があり、海洋用耐食合金の開発が要望されていた。

〔発明の目的〕

本発明の目的は前述の黄銅の脱亜鉛腐食を抑え、しかも銅イオンの長期間の溶出を確保して防食性をもたせ一般的耐食性および強度においても優れた海洋用耐食銅合金を提供するにある。

〔発明が解決しようとする問題点〕

本発明は上記目的を達成するためになされたものであり、一例としていけす金網に銅合金を使用する場合、要求される性質は

- (1) 防食性を確保するために長期にわたり銅イオンがいけす材料から溶出すること。
- (2) 銅イオンの溶出を確保するあまり、あまりに溶出量が過大とならないこと。すなわち耐食性不足で寿命が短くならぬこと。
- (3) 脱亜鉛腐食等脱成分腐食現象を起さぬこと。
- (4) 強度が強く台風等に耐え、細線化を計れること。

な皮膜が出来易くなり、銅イオン溶出量が時間の経過と共に極度に減少し、防食性に難点を生じ、脱亜鉛腐食量も多くなる。

Snは脱亜鉛腐食を抑制する効果があり、0.05重量%未満ではその効果が足りず、0.4重量%を超えるとSnの効果が飽和し、同時に加工性を損う。

なおSnとPとは夫々脱亜鉛腐食を抑制する効果があるが、共添すると脱亜鉛腐食を抑制する相乗効果を発揮する。

Niは結晶粒を微細化し耐食性を向上せしめ、更に強度をも向上させる効果があるので上記合金組成に、更にNiを添加すると本発明の効果を更に向上せしめるものである。そのNi含有量は、0.05重量%未満ではその効果が少なく、0.5重量%を超えると脱亜鉛腐食を生じ易くなる結果を得た。

以上の如く本発明の海洋用耐食銅合金の第1はZn 20～37重量%、Al 0.05～0.5重量%、Sn 0.05～0.4重量%、P 0.01～0.05重量%、残部銅及び不可避不純物からなるもので、その合金の第2は第1合金中の成分Zn、Al、Sn、Pの組

と。

(5) 加工性が良いこと。

(6) 局部腐食しにくいこと。

(7) 安価な素材であること。等があげられる。

〔問題点を解決するための手段〕

本発明者等は海洋用耐食合金の構成成分と前記要求成分との関係を鋭意研究の結果次の如き知見を得て発明に至つたものである。先ず、Znは合金の強度をあげ、素材価格を低下せしめる点で有効であり、Znを添加することによつて、銅イオンの溶出量は徐々に下がるが、下りすぎて防食性に悪影響を与える程でなく、かえつて好都合である。然しZnの添加は脱亜鉛腐食を招くので対応策が必要である。即ちZnが20重量%未満では上記利点を十分得られず、37重量%を超えると、合金の加工性が低下し、脱亜鉛腐食が著るしくなる。

Alは合金の強度をあげ、Sn及びPの添加により銅の溶出を抑制し耐食性を確保する作用がある。そしてAlが0.05重量%未満では、この効果が十分でなく、0.5重量%を超えると合金表面に強固

成に加うるにNi 0.05～0.5重量%、残部銅及び不可避不純物からなるものであり、脱亜鉛現象を抑制しうる特徴を有するものである。

以下実施例に基づいて、本発明による銅合金の効果を比較例と共に、説明する。

〔実施例〕

次の第1表に示す銅合金を各々6kg黒鉛るつぼ中で高周波溶解炉で溶解し金型に鋳込んだ。得られた鋳塊を面削した後焼鈍・圧延をくり返し最終上り圧延率が15～20%の間に入る1/2H材相当の1mm厚の板材とした。そしてこの板材について次の試験を実施した。

- ① 天然海水中で周速2 m/sの速度で回転する水車の回転物に試料をとりつけ1000時間おいた。試験前と試験後の試料の重量差から腐食量を算出しmg/日/dm<sup>2</sup>単位であらわした。
- ② 脱亜鉛試験としてISO規格に準じ75℃のCuCl<sub>2</sub>・2H<sub>2</sub>O (12.8 g/l) 溶液中に1日間浸漬した後、試料断面の10点の侵食深さを求めその最大値をμmであらわした。

③ 200mm×100mmの試験片を水深70mの実用海中に1年間浸漬し生物の付着状況を観察した。

④ 引張試験を実施し抗張力と伸びを測定した。その結果を次の第1表に示す。

第 1 表

試料番号	合 金 組 成	腐食量 (mg/d)	脱亜鉛量 (μm)	防藻性 (註)	抗張力 (kg/cm <sup>2</sup> )	伸 び (%)
実施例 1	Zn 34 P 0.03 Sn 0.22 Al 0.09 Ni 0.09	480	75	○	55	16
" 2	34 0.04 0.22 0.28 0.09	380	100	○	58	14
" 3	34 0.03 0.22 0.27 -	400	100	○	56	15
" 4	25 0.01 0.05 0.10 -	270	60	○	50	17
" 5	35 0.04 0.52 0.38 -	240	110	○△	57	14
比較例 6	30 - - -	250	440	○	46	35
" 7	35 0.02 0.21 - 0.19	490	0	○	60	11
" 8	32 0.04 0.22 0.59 0.10	180	150	×	62	9
" 9	33 0.04 0.21 0.30 0.60	360	640	○	61	8

(註) 防藻性の表示は、生物付着のなかつたもの：○ フジツボ・藤や等が表面以上ををおかつたもの：× 若干の生物付着があつたものを△であらわした。

第1表に見られるように、腐食量は脱亜鉛腐食を防止すべく添加したSnPの存在下では増加するがAlの添加により減少する傾向もある。また脱亜鉛量は比較例7に示す如く逆にSn、Pにより0となるがAlの添加により若干増加する。またAl及びNiの多量添加は脱亜鉛を招くことがわかる。防藻性はAl添加量が増えると減少する。抗張力及び伸びは比較例6に対し添加成分の多い他の合金はそれぞれ高強度低伸びの傾向を示し、Al、Ni、Znの効果が現れる。

また第1図にCu-34~35Zn-0.02~0.04P-0.21~0.22-Sn(-Ni)合金にAlを添加した場合の腐食量と脱亜鉛量とに及ぼす関係を第1表のデータからプロットした。

第1図から明らかなように本発明合金は脱亜鉛を抑制しつつ腐食量をも抑えようとするものである。

また第1表から明らかな如く、本発明合金はCuイオンの溶出によつて貝類藻類等の生物付着を防止するものであり、また黄銅の機械的強度を増し

て、強度的信頼性を増し、また継径を細くし得るなどして使用材料を減少せしめ経済性を更に向上させることをも可能である。

#### 〔発明の効果〕

本発明による海洋用銅合金は、実施例において明らかな如く、優れた耐食性、防藻性の特性をいし、取水口用格子、いけす用材料、鋼杭カバー、船舶外板等海洋環境あるいは、海水を取扱う機器において生物の付着をきらい用途の材料として好適なものである。

#### 4. 図面の簡単な説明

第1図は、本合金等Alを添加した場合の腐食量と脱亜鉛量深さを示したグラフである。

代理人 弁理士 木 村 三 朗

昭和59年9月10日

## 1. 事件の表示

特願昭59-168764

## 2. 発明の名称

海洋用耐食銅合金

## 3. 補正をする者

事件との関係 特許出願人

名称 (618) 三井金属鉱業株式会社  
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## 4. 代理人

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(6073)5. の日付 昭和 年 月 日  
(発送日 昭和 年 月 日)

## 6. 補正の対象

明細書の「発明の詳細な説明」の欄

## 7. 補正の内容

(1) 明細書第4頁第17行の「添加により」を『添加による』と補正する。

(2) 同第5頁第7行～第9行の「なおSnとPとは…発揮する。」を『Pは脱亜鉛腐食を抑える効果があり、0.01%未満ではその効果がたりず0.05%を超えるとその効果が飽和してくると同時に加工性が悪くなってくる。』と補正する。

なおSnとPとを共添すると脱亜鉛腐食を抑制する相乗効果を発揮する。』と補正する。

(3) 同第6頁第13行の「水車」を『水車状』と補正する。

(4) 同第6頁第17行の「75C」を『75℃』と補正する。

(5) 同第8頁第1表の「腐食量(mdd)」の欄の各数値

「480」 → 「48」

「380」 → 「38」

「400」 → 「40」

「270」 → 「27」

「240」 → 「24」

「250」 → 「25」

「490」 → 「49」

「180」 → 「18」

「360」 → 「36」

と夫々補正する。